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The Investigation and Assessment on Groundwater Organic Pollution

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1. Introduction

Groundwater is an important part of the water resource. It plays an irreplaceable role in supporting the national economy and social development. In China, more than 1/3 of the total water resources are utilized. As surveys shown, over 400 cities of all exploit groundwater. More seriously, many of them use groundwater as the only source of water supply.

A series of problems emerge gradually with the utilization of groundwater. Just as river waters have been over-used and polluted in many parts of the world, so have groundwater. The organic solvents and dioxins pollution of Love Canal occurred in 1978 is one of the most widely known examples, which contributes high rates of cancer and an alarming number of birth defects. Similar things occur frequently in recent decades. Governance of groundwater is so urgent a major matter of peace and prosperity. After years of researches, the nature and pollution mechanism of the contaminants in the groundwater have already got comprehended.

General scope of the organic contamination in groundwater is reviewed in this chapter. We will detail account the types of groundwater organic contamination, the pollution source of groundwater, and the fate and transport of chemicals in groundwater. Also a detailed description of the investigation and assessment method in this chapter. At last, we give some comments and suggestion on the groundwater investigation and assessment.

The figure 1 described some source of groundwater contamination, and the transport of chemicals in groundwater. We can see the landfills, leaking sewers, oil storage tanks, pesticides and fertilizer, and septic tank in the picture, all of these could be the pollution source of groundwater. We also can know the groundwater transport and flow in the unsaturated zone and saturated zone.

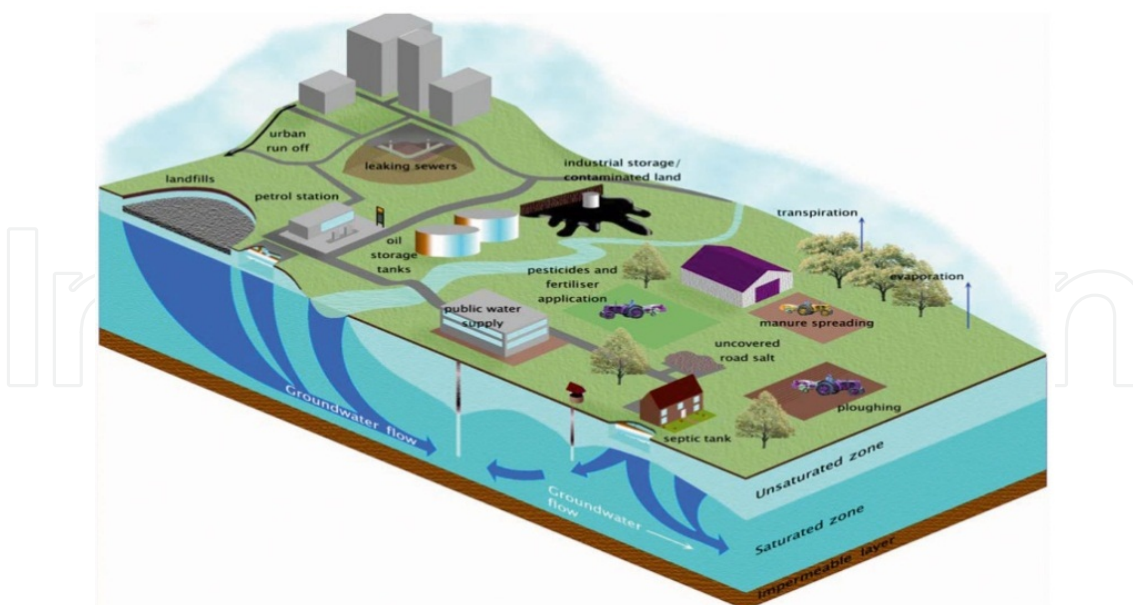


Figure 1. Diagram of the Groundwater Pollution [1].

2. A review of organic compounds in groundwater

Many studies have been conducted since 1970 to characterize concentrations of organic compounds in groundwater. In 1977, 16 drinking water wells have been closed in Gray town of Maine state because of there were at least 8 synthetic organics that were detected in drinking water wells. And in 1986, there were at least 33 organics that were detected in drinking water wells in USA [2]. It has been reported trace organic pollutants to be detected in all of 50 states. The U.S. Geological Survey(USGS) collected and assorted the test data the 1926 drinking water wells in the nation's rural areas from 1986 to 1999. And at least one VOCs were detected from 232 wells and the positive rate was 12%, with the highest positive rate were Chloroform, tetrachloroethylene and so on [3].

Similar conditions are to be found in other countries. In the 80s of last century, based on an inventory of the presence of halogenated substances in raw water of 232 groundwater pumping stations in The Netherlands a compilation of more than 100 organic substances identified in contaminated groundwater, the detection rate of trichloroethylene up to 67% [4]. The organic pollutants could be detected in groundwater in Britain. Flordward studied on 209 water supply wells in Britain shown that the main pollutant in the groundwater are the trichloroethylene and tetrachloroethylene. Beginning in 1974, Environment Agency of Japan conducted a nationwide comprehensive survey of chemical environmental safety. The trichloroethylene in groundwater was reported for the first time. The European Union is the largest pesticide consumer in the world, more than 600 pesticides were applied. Six of the top 10 were European countries in the pesticide application. Atrazine exists in groundwater

all over the Europe, and the content always beyond the European Union drinking water standard($0.1\mu\text{g/l}$) 10-100 times.

The research on organic pollutions of China is at starting stage, but there has serious organic contamination events in some areas. Based on a study of water pollution in sewage system in the Gaobeidian Prefecture of Beijing, 1988, organic substances identified in shallow wells and deep wells in South-east agriculture districts in Beijing. And 32 organic substances identified in deep wells, and 52 in shallow wells. Most of that are carcinogens (e.g. Chloroform and benzene) [5]. Analysis of the years groundwater monitoring data, and it is shown that the quality of groundwater is gradually worse.

A study on groundwater organic pollution in region of Beijing, Tianjin and Tangshan conducted by Institute of Chemistry of Chinese Academy of Sciences shows that the type of organic pollutants up to 133 [6]. The researchers Chen Honghan, He Jiangtao and others [7] have summed up the characteristics of organic contamination of shallow groundwater in a study area of the Taihu Lake basin. The results show that the detection probabilities of compounds in groundwater are higher but the concentrations of the compounds are lower. The concentrations of all the components of BTEX and halocarbons are lower than the standards set by the U.S. Environmental Protection Agency (EPA) for drinking water except for benzene in a few sampling sites.

3. Types of groundwater organic contamination

Different types of groundwater contamination sources can pose different threats to human health and different problems in health risk assessment (table 1).

3.1. Volatile organic compounds (VOCs)

Volatile organic compounds (VOCs) are organic compounds with chemical and physical properties that allow the compounds to move freely between water and air. VOCs have been used extensively in industry, commerce, and households in the United States since the 1940's. Many products contain VOCs including fuels, solvents, paints, glues, adhesives, deodorizers, refrigerants, and fumigants. In general, these compounds have low molecular weights, high vapor pressures, and low-to-medium water solubilities [8]. Many of these compounds show evidence of animal or human carcinogenicity, mutagenicity, or teratogenicity. And these compounds are quite persistent in groundwater, because of their relatively low biological and chemical reactivity. This persistence is assisted by low temperatures, absence of light and contact with the atmosphere, and comparatively low microbial concentrations typical of groundwater environments. By comparison with other organic compounds, VOCs may be transported for relatively long distances in groundwater, as a result of their relatively weak sorption affinity and their resistance to degradation. Because of human-health concerns, many VOCs have been the focus of national regulations, monitoring, and research during the past 10 to 20 years.

3.2. The pesticides

Pesticides consist of a large group of chemicals that are used in agriculture and residential settings to control plant and animal infestation. Pesticides are commonly applied on farms, fruit orchards, golf courses, and residential lawns and gardens. There are several different types of pesticides: Herbicides, Insecticides, Nematocides, Fungicides. Some pesticides do not break down easily in water and can remain in the groundwater for a long period of time. Likewise, the insecticide DDT, though banned for nearly twenty years, can still be found at trace levels in some groundwater. After prolonged exposure to high doses, some pesticides can cause cancer; some can also result in birth defects and damage to the nervous system. The use of pesticides and herbicides is one of the main ways of organic pollution of groundwater. Many water wells and irrigation wells have been closed for the byproducts from pesticides and herbicides be detected in shallow water in Colorado.

Ordering	Component	CASRN	Types
1	Trichloromethane	67-66-3	VOCs
2	Tetrachloroethylene	127-18-4	VOCs
3	1,1,1-Trichloroethane	71-55-6	VOCs
4	Trichloroethylene	79-01-6	VOCs
5	1,1-Dichloroethene	75-35-4	VOCs
6	Methyl tert-butyl ether	1634-04-4	VOCs
6*	cis-1,2-Dichloroethylene	156-59-2	VOCs
8	1, 2, 4-Trimethylbenzene	95-63-6	VOCs
9	Toluene	108-88-3	VOCs
10	Prometon	1610-18-0	Pesticides
11	1,1-Dichloroethane	75-34-3	VOCs
12	Bromacil	314-40-9	Pesticides
13	Tebuthiuron	34014-18-1	Pesticides
14	1, 3-Dichlorobenzene	541-73-1	VOCs
15	1,2-Dichloropropane	78-87-5	VOCs
16	Carbon disulfide	75-15-0	VOCs
17	Deethylatrazine	6190-65-4	Pesticides
17*	1,4-Dichlorobenzene	106-46-7	VOCs
19	Sulfamethoxazole	723-46-6	Medicine
20*	1,2-Dichlorobenzene	95-50-1	VOCs
20	2-Hydroxyatrazine	2163-68-0	Pesticides

22*	Trichlorofluoromethane	75-69-4	VOCs
22	Bentazon	25057-89-0	Pesticides
24	Atrazine	1912-24-9	Pesticides
25	Picloram	1918-2-1	Pesticides
26	Diuron	330-54-1	Pesticides
27*	Benzene	71-43-2	VOCs
27*	Tetrachloromethane	56-23-5	VOCs
29	Chlorobenzene	108-90-7	VOCs
30*	2-Butanone	78-93-3	VOCs
30	Acetone	67-64-1	VOCs
32*	m- + p-Xylene	106-42-3	VOCs
32*	trans-1,2-Dichloro- ethylen	156-60-5	VOCs
32*	1,2-Dibromoethane	106-93-4	VOCs
35	Ethylbenzene	100-41-4	VOCs
36	caffeine	58-08-2	Medicine
37	Isopropylbenzene	98-82-8	VOCs
38	o-Xylene	95-47-6	VOCs
38*	1,1,2-Trichloroethane	79-00-5	VOCs
38*	Bromodichloromethane	75-27-4	VOCs
38*	1,1,1,2-Tetrachloroethane	630-20-6	VOCs
38*	n-Propylbenzene	103-65-1	VOCs
43	Chloromethane	74-87-3	VOCs
44	1,1,2-Trichloro-1,2,2-trifluoroethane	76-13-1	VOCs
45	Dichlorodifluoromethane	75-71-8	VOCs
46	Metolachlor	51218-45-2	Pesticides
46*	Simazine	122-34-9	Pesticides
48	Bromoform	75-25-2	VOCs
48*	Imidacloprid	138261-41-3	Pesticides
48*	1,3,5-Trimethylbenzene	108-67-8	VOCs

*show the same detection with the front component. CASRN is the register number of chemical substances formulate by Chemical Abstracts Service, m means meta-position, p means para-position.

Table 1. 50 organic pollutants most commonly detected in groundwater [11]

3.3. The other organic contamination

Tens of thousands of manmade chemicals are used in today's society with all having the potential to enter our water resources. There are a variety of pathways by which these organic contaminants can make their way into the aquatic environment [9]. If the groundwater is the drinking water sources, there will be potentially dangerous on human health. Pharmaceuticals and other organic contaminants are a set of compounds that are receiving an increasing amount of public and scientific attention. Water samples were collected from a network of 47 groundwater sites across 18 states in 2000 [10]. All samples collected were analyzed for 65 organic contaminants representing a wide variety of uses and origins. Thus, sites sampled were not necessarily used as a source of drinking water but provide a variety of geohydrologic environments with potential sources of organic contaminants. Organic contaminants were detected in 81% of the sites sampled, with 35 of the 65 organic contaminants being found at least once. The most frequently detected compounds include N,N-diethyltoluamide (35%, insect repellent), bisphenol A (30%, plasticizer), tri(2-chloroethyl) phosphate (30%, fire retardant), sulfamethoxazole (23%, veterinary and human antibiotic), and 4-octylphenol monoethoxylate (19%, detergent metabolite).

4. Sources of groundwater contamination

Organic contamination includes all of natural and synthetic that could cause adverse effect on human health or ecology environment.

4.1. Natural pollution sources

Naturally formed waters such as ocean water and connate brines can be sources of groundwater contamination under certain circumstances. Changes in pumping rates can cause fresh-water aquifers to be contaminated by intrusion of seawater. Similarly, changes in the groundwater flow field or leakage through imperfectly sealed wells can cause contamination of groundwater supply by naturally occurring brines or other poor-quality waters. Generally, trace amount of natural organic compounds existence in groundwater in most of regions. The major is humic acid, especially in forest and grassland. Although itself could not impair the groundwater quality, it could be enhance the heavy metal and other organic matters activities in groundwater.

4.2. Organic contamination come from human activities

As the human population grows, groundwater pollution from human activity also increases. There are a number of possible sources that could lead to groundwater contamination. Such as crude oil leakage in oil production, organic waste discharge, spills and leaks from underground storage tank and so on.

4.2.1. City and industrial wastewater

The treatment and disposal of sewage present health risks in both developed and undeveloped countries. In undeveloped countries, sewage may be directly applied to the land surface. In more developed areas, sewage is generally transported to municipal treatment plants or disposed of in septic tanks and cesspools. Groundwater contamination can result in all these cases. Sewage provides a source of pathogens, nitrates, and a variety of organic chemicals to groundwater. Land application of sewage can provide a direct contaminant source via infiltration. Treatment plants can act as contaminant sources in several ways. Leaks may occur in sewer lines and infiltration may occur from the ponds and lagoons within the treatment plants. In addition, the sewage sludge that is a product of sewage treatment processes is often disposed on land in conjunction with agricultural activity. Depending on the characteristics of the sludge, the soil characteristics, and the application process, such land application can act as a large non-point source of groundwater contamination. Land disposal of treated waste water can pose comparable risks. Depending on hydrogeologic conditions, septic tanks and cesspools may allow untreated sewage to enter the groundwater flow system. In addition, use of solvents to clean out the systems can cause groundwater contamination by synthetic organic compounds. The material cleaned out from septic tanks must eventually be disposed of, often by land application.

Industrial Wastewaters are applied to land in ponds or lagoons that are either designed to percolate the liquid into the soil or to store and/or evaporate the liquid above ground. In either case, such facilities act as potential groundwater contamination sources. Facilities designed to intentionally infiltrate into the ground include cooling ponds for power generation and for other industrial processes. The liquids in such facilities may contain potentially hazardous materials. Storage and evaporation ponds are often lined to prevent infiltration, but are likely to act as groundwater contamination sources under some circumstances, depending on surface runoff characteristics, the integrity and permeability of the liner(s), and the groundwater flow system. Poorly designed evaporation ponds may, in many cases, function as infiltration ponds.

In the United States, the big city and small town are commonly found in contaminated groundwater. A test on 39 groundwater supply in small towns conducted by the U.S. EPA, it reported that 11 VOCs could be detected in treated or untreated groundwater [12].

4.2.2. Land disposal of municipal and industrial waste

Land disposal of solid waste is the groundwater contamination source of most current concern to the general public in many developed countries and of most current regulatory interest.

Solid waste can be disposed in landfills, facilities engineered to safely contain the waste. While landfills may often prevent exposure of solid waste at the land surface, many landfills provide a direct connection with groundwater. In the past, landfill siting was based on the availability of inexpensive, undeveloped land requiring little modification for waste disposal, rather than on hydrogeologic suitability. Disposed materials often are very susceptible to leaching into groundwater.

Landfills may be grouped according to the type of materials they contain. Municipal landfills accept only non-hazardous materials, but are still likely to contain materials which pose potential health risks. Industrial landfills may contain either "hazardous" or "non-hazardous" materials. Until recently, little was known about how they were operated or what they contained. Open dumps and abandoned disposal sites generally have no engineering design. Their connection with the groundwater system and the type of materials present is often unknown. It is often in abandoned disposal sites that large volumes of highly toxic materials are found. The most hazardous solid waste disposal generally results from industrial and manufacturing activities as well as some governmental energy and defense activities. Populations of both developed and developing countries, where there is current or historical industrial activity, face potential health risks from solid waste disposal. It is reported that there will be the highest content and most types of organic contaminants in groundwater which is near the landfills. If there has 1 kilometers distance it still exist in the groundwater [13].

4.2.3. Petrochemical pollution

In recent years, there has been increasing awareness of the large number of potentially leaking underground storage gasoline tanks. For much of the twentieth century, underground storage tanks were constructed of unprotected carbon steel. Corrosion causes leaks in such tanks over some period of time, ranging from a few years to tens of years. Although the leakage from individual tanks is often small, it is often enough to contaminate a large volume of groundwater. In addition, the large number of buried tanks-several million in the United States-makes them a potentially significant groundwater contamination source. Above ground storage tanks pose less of a threat than underground tanks. Leak detection and maintenance is easier and the connection with the groundwater system is less direct. However leaks from such tanks may still act as groundwater contamination sources.

4.2.4. Agricultural activities

Numerous agricultural activities can result in non-point sources of groundwater contamination. Fertilizers, pesticides, and herbicides are applied as part of common agricultural practice throughout the world. These applications can act as sources of contamination to groundwater supplies serving large populations. Whether or not fertilizers, pesticides, and herbicides become sources of groundwater contamination depends on changing hydrogeologic conditions, application methods, and biochemical processes in the soil. In developing countries, animal and/or human waste is used for fertilizer. This is an example of the land application of sewage discussed earlier. There are the same concerns with pathogens and nitrates. The manufactured inorganic fertilizers widely used in developed countries, and finding increasing usage in all countries, also pose the threat of nitrate contamination of groundwater systems. Pesticide and herbicide application provides a source of numerous toxic organic chemicals to groundwater supplies.

Even without the introduction of fertilizers, pesticides, and herbicides, irrigation activities can lead to groundwater contamination. Naturally occurring minerals in the soil can be leached at higher rates leading to hazardous concentration levels in the groundwater. Evap-

oration of irrigation water can cause evaporative concentration of certain chemicals in the root zone. Flushing of these chemicals can then lead to hazardous concentration levels in groundwater.

Agricultural activities related to animals also can be groundwater contamination sources. These include the feeding of animals and the storage and disposal of their waste. Animal wastes and feedlot runoff are commonly collected in some sort of pit or tank creating the contamination threat described earlier for sewage disposal.

More than 300 pesticides were applied in Asia. The Japan is a country with the largest amount of pesticide on unit area cultivated land. Indonesia, Korea, India and China are the major consumers. But, there did not have pesticides routine monitoring in the developing countries in Asia [14].

4.2.5. Surface water and atmospheric contaminants

Groundwater is but one component of the hydrologic cycle. Groundwater quality is very much influenced by surface-water conditions and vice versa. Contamination of any surface water bodies that recharge the groundwater system is a source of groundwater contamination. This includes "natural" recharge sources such as lakes and rivers as well as "man-made" recharge sources such as artificial recharge ponds/injection wells and infiltration of urban runoff. More generally, it is important to consider the interaction of all environmental sources and pathways of pollution. Environmental contaminant sources cannot be divided into separate, isolated compartments. For example, atmospheric pollution can lead to deposition of hazardous fallout to surface waters and to soils, and eventually lead to groundwater contamination.

5. The fate and transport of chemicals in groundwater

5.1. Volatilization

Volatilization occurs in whether the vadose zone or saturated zone when the dissolved contaminants and non-aqueous phase contaminants exposed to gas. The factors affecting volatilization include solubility of the compound, molecular weight and water-saturated state of the geological media. The evaporation rate must be measured fundamentally in order to determine pollutions transporting into the atmosphere, changes of the pollution load in the vadose zone and groundwater. The process that the contaminants of deep soil volatilize to the atmosphere can be assumed as one-dimensional diffusion, which can be described with Fick's second law. Volatilization of the water-soluble organic matter, such as benzene dissolved in water is generally described by Henry's Law [15].

5.2. Adsorption

Adsorption in Soil and sediment makes an important influence on the behavior of organic pollutants. The mobility and biological toxicity reduced as organics are detained in the soil

and sediment. Generally, adsorption is affected by sediments and soil properties, such as organic percentage, the type and quantity of clay minerals, cation exchange, pH and the physical and chemical properties of the contaminants. During the adsorption, the organic contaminants in the water adsorbed on the surface of the soil particles by the simultaneous distribution role of both water and solid, the driving force is mainly based on principle of "like dissolves like" and electrostatic adsorption of the polar group, and the following formulas is established [15]:

$$C_{sa} = K_a C_{wa} \quad (1)$$

The equation (1) is existed when the adsorption systems reach equilibrium. Where, C_{sa} is the amount of organic pollutants adsorbed per unit weight of soil particles; C_{wa} is concentration of organic pollutants; K_a is the total sorption coefficient.

The adsorption of organic contaminants in soil or sediment usually described by K_a (soil absorption coefficient) or K_{oc} (organic carbon absorption coefficient). The former refers to the ratio of the concentration of organic matter in the soil or sediment and its aqueous phase concentration. As well, the latter factor represents the ratio of the concentration of organic matter adsorbed by organic carbon in the soil or sediment and its aqueous phase concentration.

5.3. Biochemical processes

Microorganisms may play an important role in contamination transformations within groundwater and on the soil. They can act as catalysts for many types of reactions. When modeling biochemical reactions in groundwater, additional processes must be considered. These include the changes in the availability of substrate for the microorganisms to utilize and reactions on the particles that the microorganisms are attached to. When microbial reactions are significant, there is a possibility of clogging of pores due to precipitation reactions or to biomass accumulation [16].

Microorganisms not only influence chemical reactions, but may be contaminants themselves. There is much current uncertainty about the fate and survival time of viruses, bacteria, and larger enteric organisms in groundwater [17-18]. Distribution of microorganisms will vary greatly with depth. Potential outbreaks of waterborne diseases due to biologic pollutants are of particular concern where there is land disposal of human waste (often via septic tanks) and animal waste. The potential for transmittal of waterborne diseases in groundwater is particularly high in areas of rapid velocities such as karst regions.

Biodegradation mainly depends on two factors [19], the intrinsic characteristics of the pollutants (the structure of organics, physical and chemical properties) and microorganism (the activity of microbial populations), and the environmental factors controlling the reaction rate (temperature, pH, humidity, dissolved oxygen). As the U.S. Environmental Protection Agency researched [20], soil microbial degradation of organic pollutants can be expressed as a one-order response equation:

$$\frac{dc}{dt} = -KXC = -k_T c \quad (2)$$

Where, C is the mass fraction of soil organic matter[mg/g]; X is the number of active microbial in the organic matter of soil degradation[10⁶ /g]; t is degradation time[d]; K is the one-order biodegradation rate constant [g/(d 10⁶)]; k_r is substrate removal constant[d⁻¹].

From the above equation,

$$\frac{C}{C_0} = \exp(-KX_t) = \exp(-k_T t) \quad (3)$$

Substituted into with half-life formula,

$$t_{\frac{1}{2}} = \ln 2 / k_T \quad (4)$$

The half-life of degradation of residual contamination is determined.

5.4. Fate and transport in unsaturated zone [21]

In many cases, the receptor medium for release of a contaminant will be the unsaturated zone. In contrast to the saturated zone, pores in the unsaturated zone are not completely saturated with liquid. This fundamentally affects the processes governing flow and chemical transport. A number of processes will affect the contaminant within the unsaturated zone before it enters the saturated groundwater system and potentially is tapped by supply wells. The uncertainties in characterizing releases just described lead to uncertainties in defining the source terms and initial and boundary conditions for modeling unsaturated transport. Analogously, uncertainties in characterizing unsaturated transport processes lead to uncertainties in defining the source terms and initial and boundary conditions for modeling saturated transport.

For the most part, computer simulation of contaminant transport has focused on movement in the saturated zone. Assumptions are made regarding the time required for movement through the unsaturated zone. Often some sort of lag between source release and entry of chemicals into the saturated flow system is introduced into source terms. It is important to be aware of the unsaturated processes that are actually occurring, the uncertainty associated with these processes, and the role of monitoring in reducing these uncertainties.

5.5. Saturated transport [21]

Once a chemical has been released into the ground and has either moved through the unsaturated zone or directly entered the saturated zone, saturated transport processes will deter-

mine if, how fast, and at what concentration a chemical reaches a supply well. A great deal of research has been carried out on understanding and modeling these processes. There is increasing recognition that chemical transport must be viewed as a stochastic process.

The same elements of uncertainty are present for saturated transport as for unsaturated transport. The important differences are that in saturated transport, water content equals porosity, hydraulic conductivity is no longer a function of water content or head, gravity rather than suction head is the driving force, and the scale of concern may be much larger

6. Investigations for groundwater organic pollution

6.1. Current situation investigation

The current situation investigation main contents are as following:

Pollution source investigation: In groundwater polluted areas, investigate the non-point-source, line-source and point-source, and the type, pollution intensity, spatial distribution of natural source.

Investigation of unsaturated zone vulnerability: Investigate the unsaturated zone of thickness, lithological composition, composition, water permeability, the capability of degradation contaminations and so on.

Investigation of the pollution condition at the groundwater: Make sure the category, quantity or concentration of the pollutants, ascertain the pollution range, variation trend and the factors relation. All of these need samples collection in field and laboratory test.

6.2. Pollution source investigation

With the developed, groundwater pollution attracted wide attention. In view of existing situation, we launched the survey of pollution sources, including the following aspects: industrial pollution sources, domestic pollution sources, agricultural pollution sources and surface polluted waters.

6.2.1. Industrial pollution sources

According to industrial pollution sources, we must investigate the situation as: the company name, position, sewage, waste residue (tailings) emissions, discharge, scale, pathways and outfall location, types of pollutants, quantity, composition and hazards, and the abandoned site of major polluting enterprises, abandoned wells, oil and survey of solvents and other underground storage facilities.

6.2.2. Domestic pollution sources

The survey include the distribution of dumps, scale, waste disposal methods and effects, the generation of dump leaching filtrate and components, geological structure of storage site;

amount of sewage generated, treatment and disposal of the way, main pollutants and their concentration and hazards

6.2.3. Agricultural pollution sources

Agricultural pollution sources investigation mainly include land use history and current situation, the varieties, numbers, operations, time of farmland application of chemical fertilizers and pesticides, range of sewage irrigation, main pollutants and concentration, the number of sewage irrigation and sewage irrigation amount. The scale of farms and so on.

6.2.4. Surface polluted waters

The surface polluted waters mainly about rivers, lakes, ponds, reservoirs and drains. We survey the distribution of polluted waters, the scales, the utilizations and water quality.

The coastal areas have to survey the situation of seawater invasion and saline water distribution.

7. The assessment on groundwater organic pollution

7.1. The methods of groundwater organic pollution assessment

7.1.1. The four steps of NAS

The four steps of NAS was proposed by National Academy of Sciences, United States(NAS), was an assessment method on human health risk that led by the accident, air, water, soil and other medium. The method mainly in the following aspects: the hazard identification (qualitative evaluation the degree of hazards of the chemical substances on the human health and ecological); dose-response assessment (quantitative assessment the toxicity of chemical substances, established a relationship between the dose of chemical substances and the human health hazard); exposure assessment (quantitative or qualitative estimate or calculate the exposure, exposure frequency, exposure duration and exposure mode); exposure attribute (using the data to estimate the strength of the health hazards in the different conditions or the probability of the certain health effects). This method can qualitative analysis or quantitative analysis of groundwater contamination, or combine them, the results could be quantify and analysis, and provide more detailed information to the decision-makers.

7.1.2. The four steps of EPA

In 1989, U.S. Environmental Protection Agency (EPA) promulgated the “risk assessment guidance for superfund: Human health evaluation manual”, there was a similar assessment method to NAS method [22]. The steps following as data collection, exposure assessment, toxicity assessment, risk characterization. Contrast the two methods, NAS is more common methods, the use range wider, suitable for a variety of health risk assessment; the EPA meth-

od is more specific, it emphasis on the various parameters of the collection of contaminated sites, for the evaluation of contaminated sites, it more operational.

7.1.3. *The MMSOILS model*

The MMSOILS model is multi-media model which describe the groundwater, surface water, soil and air in the migration of chemicals, exposure and food chain accumulation [23]. Contaminate sites is multi-phase, multi-media complex. The model including the migration and transformation of pollutants module and human exposure module. Migration and transformation module include: (1)atmospheric transport pathway; (2)soil erosion; (3)groundwater migration pathway; (4)surface water pathway; (5)food chain bioaccumulation. Human exposure are: (1)adopt from drinking water, animals and plants and soil; (2)atmospheric volatiles and particulate inhalation; (3)soil, surface water and groundwater contact with skin. The model could be simulate a comprehensive migration pathway and widely used in foreign countries, and the parameters could be analysis the uncertainty.

7.1.4. *The DRASTIC method*

The DRASTIC method is a national standards system that developed by US EPA to evaluation aquifer vulnerability. It including: Depth to Water(D); Net Recharge(R); Aquifer media(A); Soil Media(S); Topography(T); Impact of the Unsaturated Zone Media(I); Conductivity of Aquifer Hydraulic(C). Assignment of each element from 1 to 10, and them proportional to the degree of vulnerability of groundwater. At the same time, each element is assigned a weight, the weight should be reflect the sensitivity of groundwater. The model can objectively assess the groundwater vulnerability of different areas, and its assumption that all regions of the aquifer has a uniform trend. But all the geological, hydrogeological and other conditions are different, and the model calculations defect, the DRASTIC method has some limitations.

7.2. Health-based risk assessment

7.2.1. *Estimating population exposure levels*

An important step in health risk assessment is the quantification of actual human exposure. Exposure can be expressed as either the total quantity of a substance that comes in contact with the human system or the rate at which a quantity of material comes in contact with the human system (mass per time or mass per time per unit body weight. The exposure assessment evaluates the type and magnitude of exposures to chemicals of potential concern at a site. The exposure assessment considers the source from which a chemical is released to the environment, the pathways by which chemicals are transported through the environmental medium, and the routes by which individuals are exposed. Parameters necessary to quantitatively evaluate dermal exposures, such as permeability coefficients, soil absorption factors, body surface area exposed, and soil adherence factors are developed in the exposure assessment. Exposure to chemicals in water can occur via direct ingestion, inhalation of vapors, or

dermal absorption. Ingestion includes drinking of fluids as well as using water for rinsing and cooking of foods. Dermal absorption includes swimming and bathing.

Determination of average exposure levels for a particular population is quite difficult. This is due to difficulties in acquiring sufficient water-quality data, in identifying the exposed individuals, and in quantifying the concentrations in the different exposure pathways. For a given groundwater contamination problem, the U.S. Environmental Protection Agency stresses the importance of identifying both the currently affected population as well as possible changes in future land use. Subpopulations that may be especially sensitive to exposure should also be identified [24].

When attempting to estimate exposure to larger population entire countries, for example other concerns arise. Cothern [25] computed the average population exposure to volatile organic compounds in the United States, based on data from several thousand ground- and surface-water supplies. National exposure was estimated as a straight extrapolation of the concentration intervals from the original data. Best- and worst-case assumptions were applied for handling the "below detectable" category. Crouch *et al.* [26] applied an alternative approach to estimate population exposure levels. Rather than estimating a distribution for exposure, they made the worst-case assumption that individuals are exposed to water at the maximum measured concentration for their water supply.

7.2.2. Health risk calculations

According to the Risk Assessment Guidance for Superfund Volume I: Human Health Evaluation Manual (Part E, Supplemental Guidance for Dermal Risk Assessment) (U.S. EPA) [27], we calculation the dermal absorbed dose (DAD) and ingestion absorbed dose (IAD) [28].

$$DAD = \frac{DA_{event} \times EV \times ED \times EF \times SA}{BW \times AT} \quad (5)$$

Where:

DAD=Dermally Absorbed Dose (mg/kg-day),

DA_{event}=Absorbed dose per event (mg/cm²-event),

SA=Skin surface area available for contact (cm²),

EV=Event frequency (events/day),

EF=Exposure frequency (days/year),

ED=Exposure duration (years),

BW=Body weight (kg),

AT=Averaging time (days).

$$IAD = \frac{\rho \times U \times EF \times ED}{BW \times AT} \quad (6)$$

Where:

IAD= Ingestion absorbed dose (mg/kg-day),

ρ = Pollutant concentration in groundwater (mg/L),

U=Drinking amount per days (L/d),

EF=Exposure frequency (days/year),

ED=Exposure duration (years),

BW=Body weight (kg),

AT=Averaging time (days).

The DAD and IAD can be represent with continuous ingestion dose (CDI).

Based on the carcinogenesis of contamination, the risk could be classified into cancer risk and noncancer hazard.

1. Noncancer hazard: Generally, the reaction of the body to non-carcinogenic substance has a dose threshold.

Lower than the threshold, they could not affect our health adversely. The non-carcinogenic risk to represent with hazard index (HI). It is defined as a ratio that continuous ingestion dose with reference dose [28].

$$HI = CDI / RfD \quad (7)$$

Where: CDI= continuous ingestion dose (mg/kg-days), RfD= reference dose (mg/kg-days).

2. Cancer risk: There does not have dose threshold for the carcinogenic. Once it exist in environments, it will affect human health adversely. Cancer risk will be represent with risk. It is defined as a product of continuous ingestion dose with carcinogenesis slope factor.

$$CDI \times SF \quad (8)$$

$$1 - \exp(-CDI \times SF) \quad (9)$$

(If the low dose exposure risk>0.01)

Where: SF= carcinogenesis slope factor ($\text{mg}^{-1} \cdot \text{kg} \cdot \text{d}$)

When calculating the risk of a variety of substances in a variety of ways, figure out all non-cancer risk and cancer risk respectively, then add all risks together. Regardless of synergistic effect and antagonistic effect.

8. The countermeasures and suggestions

8.1. The countermeasures for groundwater pollutions

Groundwater treatment technologies are mainly as follows: pump and treat, air sparging, in-situ groundwater bioremediation and in-situ reactive walls.

8.1.1. Pump and treat technology

Pump and treat is the most common form of groundwater remediation. It is often associated with treatment technologies such as Air Stripping and Liquid-phase Granular Activated Charcoal.

Pump and treat involves pumping out contaminated groundwater with the use of a submersible or vacuum pump, and allowing the extracted groundwater to be purified by slowly proceeding through a series of vessels that contain materials designed to adsorb the contaminants from the groundwater. For petroleum-contaminated sites this material is usually activated carbon in granular form. Chemical reagents such as flocculants followed by sand filters may also be used to decrease the contamination of groundwater. Air stripping is a method that can be effective for volatile pollutants such as BTEX compounds found in gasoline.

For most biodegradable materials like BTEX, MTBE and most hydrocarbons, bioreactors can be used to clean the contaminated water to non-detectable levels. With fluidized bed bioreactors it is possible to achieve very low discharge concentrations which will meet or exceed discharge standards for most pollutants.

Depending on geology and soil type, pump and treat may be a good method to quickly reduce high concentrations of pollutants. It is more difficult to reach sufficiently low concentrations to satisfy remediation standards, due to the equilibrium of absorption (chemistry)/desorption processes in the soil.

At the figure 2, we can know how does pump and treat technology work. This system usually consists of one or more wells equipped with pumps. When the pumps are turned on, they pull the polluted groundwater into the wells and up to the surface. At the surface, the water goes into a holding tank and then on to a treatment system, where it is cleaned [29].

8.1.2. Air sparging [30]

Air sparging is an in situ groundwater remediation technology that involves the injection of a gas (usually air/oxygen) under pressure into a well installed into the saturated zone. Air sparging technology extends the applicability of soil vapor extraction to saturated soils and groundwater through physical removal of volatilized groundwater contaminants and enhanced

biodegradation in the saturated and unsaturated zones. Oxygen injected below the water table volatilizes contaminants that are dissolved in groundwater, existing as a separate aqueous phase, and/or sorbed onto saturated soil particles. The volatilized contaminants migrate upward in the vadose zone, where they are removed, and generally using soil vapor extraction techniques. This process of moving dissolved and non-aqueous volatile organic compounds (VOCs), originally located below the water table, into the unsaturated zone has been likened to an in situ, saturated zone, air stripping system. In addition to this air stripping process, air sparging also promotes biodegradation by increasing oxygen concentrations in the subsurface, stimulating aerobic biodegradation in the saturated and unsaturated zones (figure 3).

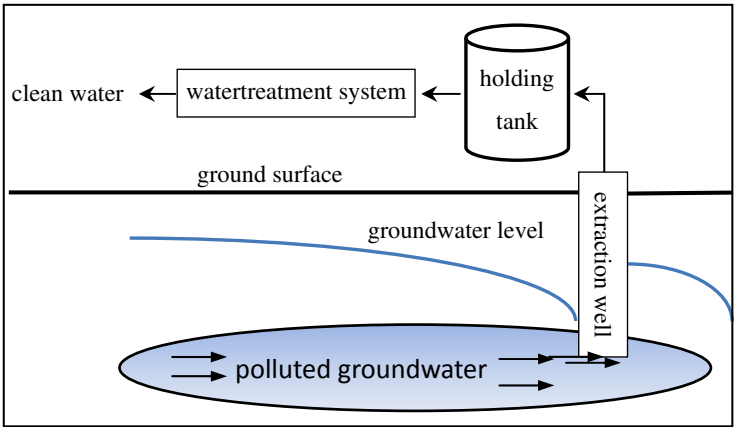


Figure 2. Pump and Treat Technology [29]

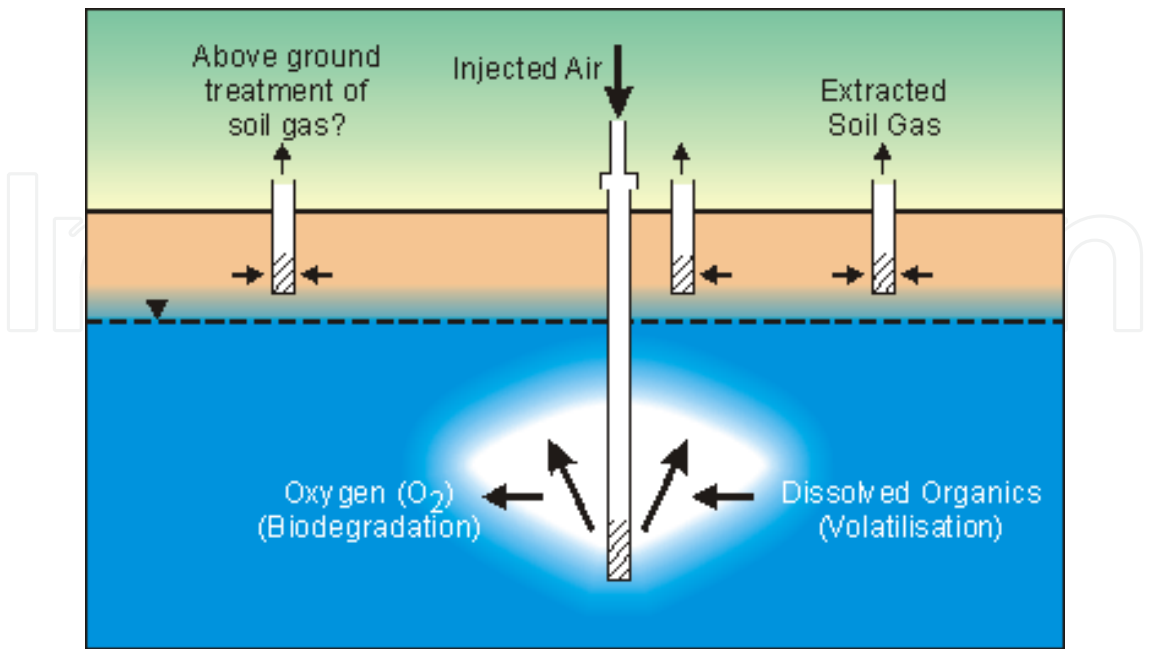


Figure 3. Air Sparging [31]

8.1.3. *In-situ groundwater bioremediation [32]*

In-situ groundwater bioremediation is a technology that encourages growth and reproduction of indigenous microorganisms to enhance biodegradation of organic constituents in the saturated zone. In-situ groundwater bioremediation can effectively degrade organic constituents which are dissolved in groundwater and adsorbed onto the aquifer matrix.

In-situ groundwater bioremediation can be effective for the full range of petroleum hydrocarbons. While there are some notable exceptions (e.g., MTBE) the short-chain, low-molecular-weight, more water soluble constituents are degraded more rapidly and to lower residual levels than are long-chain, high-molecular-weight, less soluble constituents. Recoverable free product should be removed from the subsurface prior to operation of the in-situ groundwater bioremediation system. This will mitigate the major source of contaminants as well as reduce the potential for smearing or spreading high concentrations of contaminants.

In-situ bioremediation of groundwater can be combined with other saturated zone remedial technologies (e.g., air sparging) and unsaturated zone remedial operations (e.g., soil vapor extraction, bioventing).

Bioremediation generally requires a mechanism for stimulating and maintaining the activity of these microorganisms. This mechanism is usually a delivery system for providing one or more of the following: An electron acceptor (oxygen, nitrate); nutrients (nitrogen, phosphorus); and an energy source (carbon). Generally, electron acceptors and nutrients are the two most critical components of any delivery system.

In a typical in-situ bioremediation system, groundwater is extracted using one or more wells and, if necessary, treated to remove residual dissolved constituents. The treated groundwater is then mixed with an electron acceptor and nutrients, and other constituents if required, and re-injected upgradient of or within the contaminant source. Infiltration galleries or injection wells may be used to re-inject treated water. In an ideal configuration, a "closed-loop" system would be established. All water extracted would be re-injected without treatment and all remediation would occur in situ. This ideal system would continually recirculate the water until cleanup levels had been achieved. If your state does not allow re-injection of extracted groundwater, it may be feasible to mix the electron acceptor and nutrients with fresh water instead. Extracted water that is not re-injected must be discharged, typically to surface water or to publicly owned treatment works (POTW).

8.1.4. *In-situ reactive walls [33]*

In-situ reactive walls are an emerging technology that have been evaluated, developed, and implemented only within the last few years. This technology is gaining widespread attention due to the increasing recognition of the limitations of pump and treat systems, and the ability to implement various treatment processes that have historically only been used in above-ground systems in an in situ environment. This technology is also known in the remediation industry as "funnel and gate systems" or "treatment walls".

The concept of in-situ reactive walls involves the installation of impermeable barriers downgrading of the contaminated groundwater plume and hydraulic manipulation of impacted groundwater to be directed through porous reactive gates installed within the impermeable barrier. Treatment processes designed specifically to treat the target contaminants can be implemented in these reactive or treatment gates. Treated groundwater follows its natural course after exiting the treatment gates. The flow through the treatment gates is driven by natural groundwater gradients, and hence these systems are often referred to as passive treatment walls. If a groundwater plume is relatively narrow, a permeable reactive trench can be installed across the full width of the plume, and thus preclude the necessity for installation of impermeable barriers.

In-situ reactive walls eliminate or at least minimize the need for mechanical systems, thereby reducing the long-term operation and maintenance costs that so often drive up the life cycle costs of many remediation projects. In addition, groundwater monitoring and system compliance issues can be streamlined for even greater cost savings.

Bioventing, also a modification of vapor extraction technology, is briefly contrasted with air sparging. With bioventing, extraction or injection of air into the vadose zone increases subsurface oxygen concentration, promoting bioremediation of unsaturated soil contaminants. This technique is applicable to all biodegradable contaminants, but has been applied most frequently and reportedly most successfully to sites with petroleum hydrocarbon contamination.

8.2. The suggestions for groundwater pollutions

The past 40 years, groundwater subjected to pollution, it cannot be ignored that there has a serious threat to human health and ecological security problems. The research on groundwater pollution risk assessment will help understand the relationship between the soil conditions and groundwater pollution, identify the high-risk regions of groundwater pollution, provide a powerful tools for the land use and groundwater resource management, and help the policy maker and managers to develop effective management strategies and protection measures on groundwater. So we can offer some suggestions as following:

1. Continue to strengthen the research on the fate and transport in hydrogeological conditions. Hydrogeological conditions of the contaminated sites have a vital role in organic pollution of groundwater. We should pay attention to the impact that the thickness of the unsaturated zone, the aquifer lithology of unsaturated zone and groundwater, the groundwater runoff conditions on the organic pollution investigation and contaminated aquifer restoration. Unsaturated zone is the only avenue for the organic pollutant into the groundwater system. In the protection of groundwater quality, we should take impact of the physical, chemical, and biological characteristics of the unsaturated zone soil on the transport and degradation of organic pollutants into consideration.
2. In the future research, the natural attenuation of typical organic contamination in groundwater should be reinforce research, especially the organic degradation mechanism of microbes.

3. In recent years, the environmental hormone pollution research and prevention has begun to attract the attention of the world. Environmental hormone research has become the forefront and hot topic of environmental science research. But the mechanism of environmental hormone is not clearly, we should take more attention on these.
4. The research on groundwater pollution risk assessment to be carried out on the typical regions. To provide practical experience on established an reasonable and feasible groundwater pollution risk assessment system.
5. Exerting governmental function adequately and improving the laws, regulations and norms on groundwater quality monitor and assessment. Strengthening the cross-disciplinary exchanges and studies and establishing the groundwater pollution monitor network and the chemical toxicological database.

With entering a new era of environmental protection, the research of groundwater pollution risk assessment is bound to make new contributions to human survival and to protect and improve the natural environment, and to advance the theory research of environmental science.

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